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#### (54) Title: CLEANSING COMPOSITIONS

#### (57) Abstract

A cleansing composition comprising: (a) from about 0.1 % to about 30 % by weight of an emulsifier selected from amphoteric, zwitterionic, nonionic, anionic and cationic emulsifiers and mixtures thereof; (b) from about 0.00001 % to about 5 % of an antimicrobial agent, wherein the antimicrobial agent comprises a silver compound deposited on a particulate inert support material; and (c) water. The compositions of the invention provide cleansing properties and enhanced antimicrobial efficacy.

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#### Cleansing Compositions

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#### Field of the Invention

The present invention relates to personal cleansing compositions which both cleanse the skin and which exhibit enhanced antimicrobial activity.

#### Background of the Invention

There is a continuing interest in providing consumers with personal cleansing compositions which not only cleanse the skin, but which also provide additional skin care benefits. For example, it is desirable to provide products which both thoroughly cleanse the skin and which also provide anti-acne and/or antimicrobial efficacy. This is particularly desirable for people who suffer from acne.

A wide variety of antimicrobial agents are known in the art for use in cosmetic products, e.g. phenoxyisopropanol, octopirox, zinc oxide. It is also known to use metal ions, such as silver, copper, and zinc ions for use as antimicrobial agents.

EP-A-0251753 (Johnson Matthey PLC) discloses an antimicrobial composition comprising an antimicrobial silver compound deposited on a physiologically inert oxidic synthetic material. The synthetic material is particulate, has an extended surface area, and may be selected from oxides of titanium, magnesium, aluminium, silicon, cerium, zirconium, hafnium,

niobium and tantalum as well as calcium hydroxyapatite and barium sulphate. The antimicrobial compound is described as being suitable for topical use, for impregnation of fibrous or absorbent substrates such as bandages or wound-dressings or for impregnation into medical appliances such as catheters.

It has now surprisingly been found that by incorporating antimicrobial agents of the type disclosed in EP-A-0251783 into cleansing compositions, compositions are provided which provide cleansing properties and improved anti-acne and antimicrobial efficacy at very low levels of antimicrobial active, i.e. lower levels than generally used with, for example, phenoxyisopropanol or octopirox.

#### Summary of the Invention

Hence according to the present invention there is provided a cleansing composition comprising:

- (a) from about 0.1% to about 30% by weight of an emulsifier selected from amphoteric, zwitterionic, nonionic, anionic and cationic emulsifiers and mixtures thereof;
- (b) from about 0.0001% to about 5% of an antimicrobial agent, wherein the antimicrobial agent comprises a silver compound deposited on an inert particulate support material; and;
- (c) water.

The compositions of the invention provide cleansing efficacy and enhanced antimicrobial and/or anti-acne efficacy.

#### **Detailed Description of the Invention**

The compositions of the present invention comprise emulsifier, antimicrobial agent and water.

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A first essential ingredient of the compositions of the present invention is an emulsifier. The emulsifier is present in the compositions herein at a level of from about 0.1% to about 30%, preferably from about 1% to about 20%, more preferably from about 1% to about 15% by weight of composition. Even though the term "emulsifier" is used herein to describe these materials, this term is not intended to exclude those emulsifiers which also have surfactant properties.

The emulsifier is selected from amphoteric, zwitterionic, nonionic, anionic and cationic surfactants and mixtures thereof. Suitable emulsifiers for use herein are disclosed in prior patents and other references. See McCutcheon's, Detergents and Emulsifiers, North American Edition (1986), published by Allured Publishing Corporation; US-A-5011681, US-A-4421769 and US-A-3755560.

The exact emulsifier chosen will depend upon the pH of the composition and the other components present. Suitable emulsifier types include tetra-alkyl ammonium salts, esters of glycerin, esters of propylene glycol, fatty acid esters of polyethylene glycol, fatty acid esters of polypropylene glycol, esters of sorbitol, esters of sorbitan anhydrides, carboxylic acid copolymers, esters and ethers of glucose, ethoxylated ethers, ethoxylated alcohols, alkyl phosphates, polyoxyethylene fatty ether phosphates, fatty acid amides, acyl lactylates, soaps and mixtures thereof.

Suitable herein, especially when the emulsions have a pH from about 2 to about 7, are cationic emulsifiers. A wide variety of cationic emulsifiers and surfactants useful herein are disclosed in U.S. Patent No. 5,151,209, to McCall et al., issued September 29, 1992; U.S. Patent No. 5,151,210, to Steuri et al., issued September 29, 1992; U.S. Patent No. 5,120,532, to Wells et al., issued June 9, 1992; U.S. Patent No. 4,387,090, to Bolich, issued June 7, 1983;; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent No. 3,929,678, to Laughlin et al., issued December 30, 1975; U.S. Patent No. 3,959,461, to Bailey et al., issued May 25, 1976; McCutcheon's. Detergents & Emulsifiers, (North American edition 1979) M.C. Publishing Co.; and Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; all of these documents being incorporated herein by reference in their

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entirety. The cationic emulsifiers useful herein include cationic ammonium salts such as those having the formula:

wherein R<sub>1</sub>, is selected from an alkyl group having from about 12 to about 22 carbon atoms, or aromatic, aryl or alkaryl groups having from about 12 to about 22 carbon atoms; R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are independently selected from hydrogen, an alkyl group having from about 1 to about 22 carbon atoms, or aromatic, aryl or alkaryl groups having from about 12 to about 22 carbon atoms; and X is an anion selected from chloride, bromide, iodide, acetate, phosphate, nitrate, sulfate, methyl sulfate, ethyl sulfate, tosylate, lactate, citrate, glycolate, and mixtures thereof. Additionally, the alkyl groups can also contain ether linkages, or hydroxy or amino group substituents (e.g., the alkyl groups can contain polyethylene glycol and polypropylene glycol moieties).

More preferably, R<sub>1</sub> is an alkyl group having from about 12 to about 22 carbon atoms; R<sub>2</sub> is selected from H or an alkyl group having from about 1 to about 22 carbon atoms; R<sub>3</sub> and R<sub>4</sub> are independently selected from H or an alkyl group having from about 1 to about 3 carbon atoms; and X is as described in the previous paragraph.

Most preferably, R<sub>1</sub> is an alkyl group having from about 12 to about 22 carbon atoms; R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are selected from H or an alkyl group having from about 1 to about 3 carbon atoms; and X is as described previously.

Alternatively, other useful cationic emulsifiers include amino-amides, wherein in the above structure R<sub>1</sub> is alternatively R<sub>5</sub>CO-(CH<sub>2</sub>)<sub>n</sub>, wherein R<sub>5</sub> is an alkyl group having from about 12 to about 22 carbon atoms, and n is an integer from about 2 to about 6, more preferably from about 2 to about 4, and most preferably from about 2 to about 3. Nonlimiting examples of these cationic emulsifiers include stearamidopropyl PG-dimonium chloride phosphate, stearamidopropyl ethyldimonium ethosulfate, stearamidopropyl dimethyl (myristyl acetate) ammonium

· : chloride, stearamidopropyl dimethyl cetearyl ammonium tosylate, stearamidopropyl dimethyl ammonium chloride, stearamidopropyl dimethyl ammonium lactate, and mixtures thereof.

Nonlimiting examples of quaternary ammonium salt cationic emulsifiers include those selected from the group consisting of cetyl ammonium chloride, cetyl ammonium bromide, lauryl ammonium chloride, lauryl ammonium bromide, stearyl ammonium chloride, stearyl ammonium bromide, cetyl dimethyl ammonium chloride, cetyl dimethyl ammonium bromide, lauryl dimethyl ammonium chloride, lauryl dimethyl ammonium bromide, stearyl dimethyl ammonium chloride, stearyl dimethyl ammonium bromide, cetyl trimethyl ammonium chloride, cetyl trimethyl ammonium bromide, lauryl trimethyl ammonium chloride, lauryl trimethyl ammonium bromide, stearyl trimethyl ammonium chloride, stearyl trimethyl ammonium bromide, lauryl dimethyl ammonium chloride, stearyl dimethyl cetyl ditallow dimethyl ammonium chloride, dicetyl ammonium chloride, dicetyl ammonium bromide, dilauryl ammonium chloride, dilauryl ammonium bromide, distearyl ammonium chloride, distearyl ammonium bromide, dicetyl methyl ammonium chloride, dicetyl methyl ammonium bromide, dilauryl methyl ammonium chloride, dilauryl methyl ammonium bromide, distearyl methyl ammonium chloride, distearyl methyl ammonium bromide, and mixtures thereof. Additional quaternary ammonium salts include those wherein the C12 to C22 alkyl carbon chain is derived from a tallow fatty acid or from a coconut fatty acid. The term "tallow" refers to an alkyl group derived from tallow fatty acids (usually hydrogenated tallow fatty acids), which generally have mixtures of alkyl chains in the C16 to C18 range. The term "coconut" refers to an alkyl group derived from a cocunt fatty acid, which generally have mixtures of alkyl chains in the C12 to C14 range. Examples of quaternary ammonium salts derived from these tallow and cococut sources include ditallow dimethyl ammonium chlroide, ditallow dimehtyl ammonium methyl sulfate, di(hydrogenated tallow) dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl)dimethyl ammonium chloride, di(coconutalkyl)dimethyl ammonium bromide, tallow ammonium chloride, coconut ammonium chloride, stearamidopropyl PG-dimonium chloride phosphate, stearamidopropyl ethyldimonium ethosulfate, stearamidopropyl dimethyl

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(myristyl acetate) ammonium chloride, stearamidopropyl dimethyl cetearyl ammonium tosylate, stearamidopropyl dimethyl ammonium chloride, stearamidopropyl dimethyl ammonium lactate, and mixtures thereof.

More preferred cationic emulsifiers are those selected from the group consisting of dilauryl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, dimyristyl dimethyl ammonium chloride, dipalmityl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, stearamidopropyl PG-dimonium chloride phosphate, stearamidopropyl ethyldimonium ethosulfate, stearamidopropyl dimethyl (myristyl acetate) ammonium chloride, stearamidopropyl dimethyl cetearyl ammonium tosylate, stearamidopropyl dimethyl ammonium chloride, stearamidopropyl dimethyl ammonium chloride, stearamidopropyl dimethyl ammonium chloride, stearamidopropyl dimethyl ammonium lactate, and mixtures thereof.

Most preferred cationic emulsifiers are those selected from the group consisting of dilauryl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, dimyristyl dimethyl ammonium chloride, dipalmityl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, and mixtures thereof.

Also, preferred for use herein are certain nonionic emulsifiers, especially when used in combination with the cationic emulsifiers described above. It has been found that a blend of a high HLB nonionic emulsifier with a low HLB nonionic emulsifer is especially preferred. Without being limited by theory, it is believed that this combination of both high and low HLB nonionic emulsifiers provides compositions demonstrating enhanced emulsion stability. The abbreviation "HLB" stands for hydrophilic lipophilic balance. The HLB system is well known in the art and is described in detail in "The HLB System, A Time-Saving Guide to Emulsifier Selection", ICI Americas Inc., August 1984, which is incorporated herein by reference.

As defined herein the high HLB nonionic emulsifiers include any of the well-known nonionic emulsifiers that have an HLB of from about 6 to about 18, preferably from about 8 to about 18, and more preferably from about 10 to about 18. These high HLB nonionic emulsifiers do not include those emulsifiers with HLB values less than 6, as described below. Typical of these high HLB nonionic emulsifiers are ethoxylated or

· . propoxylated, preferably ethoxylated, alcohols and alkyl phenols, with the alcohol derivatives being preferred. In general, these alcohol derivatives contain a straight or branched chain alkyl group in the C<sub>8-22</sub>, preferably C<sub>10-20</sub>, more preferably C<sub>12-20</sub>, range and generally contain from about 6 to about 30, preferably from about 6 to about 25, ethylene oxide or propylene oxide groups. Among these ethoxylated and propoxylated alcohols, the ethoxylated derivatives are most preferred. Preferred for use herein are polyethylene oxide ethers derived from lauryl alcohol, cetyl alcohol, oleyl alcohol, stearyl alcohol, isostearyl alcohol, myristyl alcohol, behenyl alcohol, and mixtures thereof. More preferred for use herein are: polyoxyethylene 10 cetyl ether, known by the CTFA designation as ceteth-10; polyoxyethylene (21) stearyl ether, known by the CTFA designation steareth-21; coconut alkyl polyethoxylate (6.5); decyl polyethoxylate (6); and mixtures thereof. Most preferred for use herein are ceteth-10, steareth-21, and mixtures thereof.

Detailed listings of high HLB nonionic emulsifiers can be found in McCutcheon's EMULSIFIERS AND DETERGENTS, North American Edition, 1984, McCutcheon Division, MC Publishing Company, which has already been incorporated herein by reference.

The low HLB nonionic emulsifiers are defined herein as any of the well known nonionic emulsifiers having an HLB value from about 1 to about, but not greater than or equal to, 6. These low HLB nonionic emulsifiers do not include the high HLB nonionic emulsifier described above.

Examples of these low HLB nonionic emulsifiers are ethoxylated alcohols with the alcohol derivatives being preferred. In general, these alcohol derivatives contain a straight or branched chain alkyl group in the C preferably C more preferably C range, and generally contain from about 1 to about 5 ethylene oxide groups per molecule.

Some nonlimiting examples of these low HLB nonionic emulsifiers useful herein include stearic acid ethoxylated with 1 mole of ethylene oxide (i.e. steareth-1), steareth-2, steareth-3, steareth-4, steareth-5, ceteth-1, cetheth-2, ceteth-3, ceteth-4, ceteth-5, laureth-1, laureth-2, laureth-3, laureth-4, laureth-5, and mixtures thereof. Preferred low HLB nonionic emulsifiers are steareth-1, steareth-2, steareth-3, ceteth-1, ceteth-2, cetheth-3, laureth-

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1, laureth-2, laureth-3, and mixtures thereof. More preferred are steareth-2, ceteth-2, laureth-2, and mixtures thereof. Most preferred is steareth-2, which is available commercially as Brij 72 from ICI Americas.

Detailed listings of low HLB emulsifiers can be found in McCutcheon's EMULSIFIERS AND DETERGENTS, North American Edition, 1984, McCutcheon Division, MC Publishing Company, which has already been incorporated herein by reference.

In the present invention, it has been found that when a combination of a high and a low HLB nonionic emulsifer are used together, that the combination of steareth-21 and/or ceteth-10 with steareth-2 is preferred.

Amphoteric surfactants suitable for use in the compositions of the invention include:

(a) imidazolinium surfactants of formula (III)

wherein R<sub>1</sub> is C<sub>7</sub>-C<sub>22</sub> alkyl or alkenyl, R<sub>2</sub> is hydrogen or CH<sub>2</sub>Z, each Z is independently CO<sub>2</sub>M or CH<sub>2</sub>CO<sub>2</sub>M, and M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium; and/or ammonium derivatives of formula (IV)

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$$\begin{smallmatrix} \mathsf{C}_2\mathsf{H}_4\mathsf{OH} \\ \mathsf{R}_1\mathsf{CONH}\,(\mathsf{CH}_2)_{2}^{\mathsf{N}^+}\mathsf{CH}_2\mathsf{Z} \\ \mathsf{R}_2 \end{smallmatrix}$$

wherein R<sub>1</sub>, R<sub>2</sub> and Z are as defined above;

(b) aminoalkanoates of formula (V)

#### $R_1NH(CH_2)_nCO_2M$

iminodialkanoates of formula (VI)

 $R_1N[(CH_2)_mCO_2M]_2$ 

and iminopolyalkanoates of formula (VII)

 $R_{1-}[N(CH_2)_p]_qN[CH_2CO_2M]_2$   $CH_2CO_2M$ 

wherein n, m, p, and q are numbers from 1 to 4, and  $R_1$  and M are independently selected from the groups specified above; and

#### (c) mixtures thereof.

Suitable amphoteric surfactants of type (a) are marketed under the trade name Miranol and Empigen and are understood to comprise a complex mixture of species. Traditionally, the Miranols have been described as having the general formula III, although the CTFA Cosmetic Ingredient Dictionary, 3rd Edition indicates the non-cyclic structure IV while the 4th Edition indicates yet another structural isomer in which R<sub>2</sub> is O-linked rather than N-linked. In practice, a complex mixture of cyclic and non-cyclic species is likely to exist and both definitions are given here for sake of completeness. Preferred for use herein, however, are the non-cyclic species.

Examples of suitable amphoteric surfactants of type (a) include compounds of formula III and/or IV in which  $R_1$  is  $C_8H_{17}$  (especially iso-capryl),  $C_9H_{19}$  and  $C_{11}H_{23}$  alkyl. Especially preferred are the compounds in which  $R_1$  is  $C_9H_{19}$ , Z is  $CO_2M$  and  $R_2$  is H; the compounds in which  $R_1$  is  $C_{11}H_{23}$ , Z is  $CO_2M$  and  $R_2$  is  $CH_2CO_2M$ ; and the compounds in which  $R_1$  is  $C_{11}H_{23}$ , Z is  $CO_2M$  and  $R_2$  is H.

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In CTFA nomenclature, materials suitable for use in the present invention include cocoamphocarboxypropionate, cocoamphocarboxy propionic acid, and especially cocoamphoacetate and cocoamphodiacetate (otherwise referred to as cocoamphocarboxyglycinate). Specific commercial products include those sold under the trade names of Ampholak 7TX (sodium carboxy methyl tallow polypropyl amine), Empigen CDL60 and CDR 60 (Albright & Wilson), Miranol H2M Conc. Miranol C2M Conc. N.P., Miranol C2M Conc. O.P., Miranol C2M SF, Miranol CM Special (Rhône-Poulenc); Alkateric 2CIB (Alkaril Chemicals); Amphoterge W-2 (Lonza, Inc.); Monateric CDX-38, Monateric CSH-32 (Mona Industries); Rewoteric AM-2C (Rewo Chemical Group); and Schercotic MS-2 (Scher Chemicals).

It will be understood that a number of commercially-available amphoteric surfactants of this type are manufactured and sold in the form of electroneutral complexes with, for example, hydroxide counterions or with anionic sulfate or sulfonate surfactants, especially those of the sulfated C8-C18 alcohol, C8-C18 ethoxylated alcohol or C8-C18 acyl glyceride types. Preferred from the viewpoint of mildness and product stability, however, are compositions which are essentially free of (non-ethoxylated) sulfated alcohol surfactants. Note also that the concentrations and weight ratios of the amphoteric surfactants are based herein on the uncomplexed forms of the surfactants, any anionic surfactant counterions being considered as part of the overall anionic surfactant component content.

Examples of preferred amphoteric surfactants of type (b) include N-alkyl polytrimethylene poly-, carboxymethylamines sold under the trade names Ampholak X07 and Ampholak 7CX by Berol Nobel and also salts, especially the triethanolammonium salts and salts of N-lauryl-beta-amino propionic acid and N-lauryl-imino-dipropionic acid. Such materials are sold under the trade name Deriphat by Henkel and Mirataine by Rhône-Poulenc.

The compositions herein can also contain from about 0.1% to about 20%, more preferably from about 0.1% to about 10%, and especially from about 1% to about 8% of a zwitterionic surfactant.

Water-soluble auxiliary betaine surfactants suitable for inclusion in the compositions of the present invention include alkyl betaines of the formula  $R_5R_6R_7N^+$  (CH<sub>2</sub>)<sub>n</sub>CO<sub>2</sub>M (VIII) and amido betaines of the formula (IX)

$$R_5$$
CON(CH<sub>2</sub>)<sub>m</sub>N(CH<sub>2</sub>)<sub>n</sub>CO<sub>2</sub>M

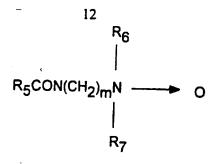
wherein R<sub>5</sub> is C<sub>11</sub>-C<sub>22</sub> alkyl or alkenyl, R<sub>6</sub> and R<sub>7</sub> are independently C<sub>1</sub>-C<sub>3</sub> alkyl, M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium, and n, m are each numbers from 1 to 4. Preferred betaines include cocoamidopropyldimethylcarboxymethyl betaine, laurylamidopropyldimethylcarboxymethyl betaine and Tego betaine (RTM).

Water-soluble auxiliary sultaine surfactants suitable for inclusion in the compositions of the present invention include alkyl sultaines of the formula (X);

$$\begin{array}{c} \mathsf{R}_2 \\ | \\ \mathsf{R}_1\mathsf{CON}(\mathsf{CH}_2)_\mathsf{m}\mathsf{N}^+(\mathsf{CH}_2)\mathsf{n}\mathsf{CH}(\mathsf{OH})\mathsf{CH}_2\mathsf{SO}_3^-\mathsf{M}^+ \\ | \\ \mathsf{R}_3 \end{array}$$

wherein R<sub>1</sub> is C<sub>7</sub> to C<sub>22</sub> alkyl or alkenyl, R<sub>2</sub> and R<sub>3</sub> are independently C<sub>1</sub> to C<sub>3</sub> alkyl, M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium and m and n are numbers from 1 to 4. Preferred for use herein is coco amido propylhydroxy sultaine.

Water-soluble auxiliary amine oxide surfactants suitable for inclusion in the compositions of the present invention include alkyl amine oxide R5R6R7NO and amido amine oxides of the formula (XI)



wherein R<sub>5</sub> is C<sub>11</sub> to C<sub>22</sub> alkyl or alkenyl, R<sub>6</sub> and R<sub>7</sub> are independently C<sub>1</sub> to C<sub>3</sub> alkyl, M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium and m is a number from 1 to 4. Preferred amine oxides include cocoamidopropylamine oxide, lauryl dimethyl amine oxide and myristyl dimethyl amine oxide.

Suitable anionic surfactants suitable for use herein can generally be described as mild synthetic detergent surfactants and include ethoxylated alkyl sulfates, alkyl glyceryl ether sulfonates, methyl acyl taurates, fatty acyl glycinates, N-acyl glutamates, acyl isethionates, alkyl sulfosuccinates, alpha-sulfonated fatty acids, their salts and/or their esters, alkyl ethoxy carboxylates, alkyl phosphate esters, ethoxylated alkyl phosphate esters, acyl sarcosinates and fatty acid/protein condensates, and mixtures thereof. Alkyl and/or acyl chain lengths for these surfactants are C8-C22, preferably C10-C18 more preferably C12-C14.

Preferred for use herein from the viewpoint of optimum mildness and lathering characteristics are the salts of sulfuric acid esters of the reaction product of 1 mole of a higher fatty alcohol and from about 1 to about 12 moles of ethylene oxide, with sodium and magnesium being the preferred counterions. Particularly preferred are the alkyl sulfates containing from about 2 to 6, preferably 2 to 4 moles of ethylene oxide, such as sodium laureth-2 sulfate, sodium laureth-3 sulfate and magnesium sodium laureth-3.6 sulfate. In preferred embodiments, the anionic surfactant contains at least about 50%, especially at least about 75% by weight of ethoxylated alkyl sulfate.

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In preferred embodiments herein, the compositions comprise a mixture of anionic and betaine emulsifiers, preferably in a ratio of betaine: anionic in the range of from about 5:1 to about 1:1.

A second essential ingredient of the compositions herein is an antimicrobial agent. The antimicrobial agent herein is in the form of a silver compound deposited on an inert particulate support material. Preferably the support material is selected from oxides of titanium, magnesium, aluminium, silicon, cerium, zirconium, hafnium, niobium, and tantalum, calcium hydroxyapatite and barium sulphate. Preferably said silver compound is selected from AgCl, AgBr, Ag2CO3, AgOH and Ag3PO4. The antimicrobial agent is present in the compositions herein in an amount of from about 0.0001% to about 5%, preferably from about 0.0001% to about 3%, more preferably from about 0.0001% to about 1%, and especially from about 0.0001% to about 0.1% by weight of composition. Preferably in emulsion compositions, the antimicrobial agent is present in the water phase.

Most preferably the support material is titanium dioxide, preferably in one or more of the crystalline forms anatase, rutile or brookite.

Suitably, such antimicrobial agents may be prepared by suspending the support material in an aqueous solution of a soluble metal compound and reacting this suspension with a compound containing the anion of a desired antimicrobial metal salt. For example, titanium dioxide may be suspended in an aqueous solution of silver nitrate and reacted with silver chloride to precipitate silver chloride on the titanium dioxide. An example of this process is described in EP-A-0251783 (Johnson Matthey PLC) which is herein incorporated by way of reference.

The antimicrobial metal source may be employed alone or in combination with further antimicrobial agents, for instance zinc salts such as zinc oxide, and organic antimicrobial agents such as piroctone olamine and phenoxyisopropanol.

The antimicrobial metal source, i.e. the silver compound, may be present in an amount of from about 0.5% to about 75%, preferably from about 0.5% to about 50%, and especially from about 5% to about 30% by weight of the antimicrobial agent.

Preferably, the particulate support material has an average particle size of less than about 25 micrometres. Suitably, the particle size is between about 0.01 and 15 micrometres. Suitably, the particles have an open morphology. Preferably each particle comprises an agglomeration of crystallites having open spaces between the crystallites. Suitably the particles are roughly spherical clusters of crystallites. Preferably the particles exhibit some irregularity of shape. Where titanium dioxide is used to provide the crystallites, the primary crystal size will preferably be between 0.005 micrometres and 5 micrometres, preferably between 0.01 micrometres and 1 micrometre.

Preferably, the support material has a mean surface area of from about 1 to about 300m2/g.

A preferred antimicrobial agent for use herein is JMAC TD supplied by Johnson Matthey. Also suitable for use herein is JMAC also supplied by Johnson Matthey.

The compositions herein preferably further comprise from about 0.1% to about 10%, preferably from about 0.1% to about 5%, especially from about 1% to about 3% by weight of skin care active. Examples of useful skin care actives include the keratolytics such as salicylic acid, and resorcinol; retinoids such as retinoic acid and its derivatives (e.g., cis and trans); antibiotics and antimicrobials such as benzoyl peroxide, octopirox, erythromycin and its metal complexes (e.g., zinc erythromycin), tetracyclin, 2,4,4'-trichloro-2'-hydroxy diphenyl ether, 3,4,4'-trichlorobanilide, azelaic acid and its derivatives, phenoxyethanol, phenoxypropanol, phenoxyisopropanol, ethyl acetate, clindamycin and meclocycline; sebostats such as flavinoids; alpha and beta hydroxy acids; and bile salts such as scymol sulfate and its derivatives, deoxycholate, and cholate.

Some of the above listed actives can also be used as anti-wrinkle and anti-skin atrophy actives, e.g. retinoic acid and salicylic acid.

Other suitable active agents for inclusion in the compositions of the invention include non-steroidal anti-inflammatory actives (NSAIDS): Examples of NSAIDS include the following categories: propionic acid derivatives; acetic acid derivatives; fenamic acid derivatives; biphenylcarboxylic acid derivatives; and oxicams. All of these NSAIDS are fully described in the U.S. Patent 4,985,459 to Sunshine et al., issued January 15, 1991, incorporated by reference herein. Examples of useful NSAIDS include acetyl salicylic acid, acetaminophen, ibuprofen, naproxen, benoxaprofen, flurbiprofen, fenoprofen, fenbufen, ketoprofen, indoprofen, pirprofen, carprofen, oxaprozin, pranoprofen, miroprofen, tioxaprofen, suprofen, alminoprofen, tiaprofenic acid, fluprofen and bucloxic acid. Also useful are the steroidal anti-inflammatory drugs including hydrocortisone and the like. Topical anesthetics: Examples of topical anesthetic drugs include lidocaine, bupivacaine, chlorprocaine, dibucaine, etidocaine, mepivacaine, tetracaine, dyclonine, hexylcaine, procaine, cocaine, ketamine, pramoxine, phenol, and pharmaceutically acceptable salts thereof. Antimicrobial and antifungal actives: Examples of antimicrobial and antifungal actives include b-lactam drugs, quinolone drugs, ciprofloxacin, norfloxacin, tetracycline, erythromycin, amikacin, 2,4,4'-trichloro-2'-hydroxy diphenyl ether, 3,4,4'trichlorobanilide, phenoxyethanol, phenoxy propanol, phenoxyisopropanol, doxycycline, capreomycin, chlorhexidine, chlortetracycline, oxytetracycline, clindamycin, ethambutol, hexamidine isethionate, metronidazole, pentamidine, gentamicin, kanamycin, lineomycin, methacycline, methenamine, minocycline, neomycin, netilmicin, paromomycin, streptomycin, tobramycin, miconazole, tetracycline hydrochloride, erythromycin, zinc erythromycin, erythromycin estolate, erythromycin stearate, amikacin sulfate, doxycycline hydrochloride, capreomycin sulfate, chlorhexidine gluconate, chlorhexidine hydrochloride, chlortetracycline hydrochloride, oxytetracycline hydrochloride, clindamycin hydrochloride, ethambutol hydrochloride, metronidazole hydrochloride, pentamidine hydrochloride, gentamicin sulfate, kanamycin sulfate, lineomycin hydrochloride, methacycline hydrochloride, methenamine hippurate, methenamine mandelate, minocycline hydrochloride, neomycin sulfate, netilmicin

sulfate, paromomycin sulfate, streptomycin sulfate, tobramycin sulfate, miconazole hydrochloride, amanfadine hydrochloride, amanfadine sulfate, octopirox, parachlorometa xylenol, nystatin, tolnaftate and clotrimazole.

Sunscreening actives: A wide variety of sunscreening actives are useful herein, and include those described in U.S. Patent No. 5,087,445, to Haffey et al., issued February 11, 1992; U.S. Patent No. 5,073,372, to Turner et al., issued December 17, 1991; U.S. Patent No. 5,073,371, to Turner et al. issued December 17, 1991; and Segarin, et al., at Chapter VIII, pages 189 et seq., of Cosmetics Science and Technology, all of which are incorporated herein by reference in their entirety. Nonlimiting examples of sunscreen actives include those selected from the group consisting of 2-ethylhexyl p-methoxycinnamate, 2-ethylhexyl N,Ndimethyl-p-aminobenzoate, p-aminobenzoic acid, 2-phenylbenzimidazole-5-sulfonic acid, octocrylene, oxybenzone, homomenthyl salicylate, octyl salicylate, 4,4'-methoxy-t-butyldibenzoylmethane, 4-isopropyl dibenzoylmethane, 3-benzylidene camphor, 3-(4-methylbenzylidene) camphor, and mixtures thereof. Still other useful sunscreens are those disclosed in U.S. Patent No. 4,937,370, to Sabatelli, issued June 26, 1990; and U.S. Patent No. 4,999,186, to Sabatelli et al., issued March 12, 1991; these two references are incorporated by reference herein in their entirety. The sunscreening agents disclosed therein have, in a single molecule, two distinct chromophore moieties which exhibit different ultraviolet radiation absorption spectra. One of the chromophore moieties absorbs predominantly in the UVB radiation range and the other absorbs strongly in the UVA radiation range. These sunscreening agents provide higher efficacy, broader UV absorption, lower skin penetration and longer lasting efficacy relative to conventional sunscreens. Especially preferred examples of these sunscreens include those selected from the group consisting of 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester of 2,4dihydroxybenzophenone, 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester with 4-hydroxydibenzoylmethane, 4-N,N-(2ethylhexyl)methylaminobenzoic acid ester of 2-hydroxy-4-(2hydroxyethoxy)benzophenone, 4-N,N-(2-ethylhexyl)-methylaminobenzoic acid ester of 4-(2-hydroxyethoxy)dibenzoylmethane, and mixtures thereof.

Preferred examples of actives useful herein include those selected from the group consisting of salicylic acid, 3-hydroxy benzoic acid, 4-hydroxy

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benzoic acid, acetyl salicylic acid, 2-hydroxybutanoic acid, 2hydroxypentanoic acid, 2-hydroxyhexanoic acid, cis-retinoic acid, transretinoic acid, azelaic acid, arachidonic acid, benzoylperoxide, tetracyclin, ibuprofen, naproxen, hydrocortisone, acetominophen, erythromycin, zinc erythromycin, resorcinol, phenoxyethanol, phenoxypropanol, phenoxyisopropanol, 2,4,4'-trichloro-2'-hydroxy diphenyl ether, 3,4,4'trichlorocarbanilide, octopirox, lidocaine hydrochloride, clotrimazole, miconazole, neocycin sulfate, 2-ethylhexyl p-methoxycinnamate, 2ethylhexyl N,N-dimethyl-p-aminobenzoate, p-aminobenzoic acid, 2phenylbenzimidazole-5-sulfonic acid, octocrylene, oxybenzone, homomenthyl salicylate, octyl salicylate, 4,4'-methoxy-tbutyldibenzoylmethane, 4-isopropyl dibenzoylmethane, 3-benzylidene camphor, 3-(4-methylbenzylidene) camphor, 4-N,N-(2ethylhexyl)methylaminobenzoic acid ester of 2,4-dihydroxybenzophenone, 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester with 4hydroxydibenzoylmethane, 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester of 2-hydroxy-4-(2-hydroxyethoxy)benzophenone, 4-N,N-(2ethylhexyl)-methylaminobenzoic acid ester of 4-(2hydroxyethoxy)dibenzoylmethane, and mixtures thereof. More preferred examples of actives useful herein include those selected from the group consisting of salicylic acid, acetyl salicylic acid, cis-retinoic acid, transretinoic acid, azelaic acid, tetracyclin, ibuprofen, naproxen, acetominophen, hydrocortisone, erythromycin, zinc erythromycin, resorcinol, phenoxyethanol, phenoxypropanol, phenoxyisopropanol, 2,4,4'-trichloro-2'-hydroxy diphenyl ether, 3,4,4'-trichlorocarbanilide, octopirox, 2-ethylhexyl p-methoxycinnamate, 2-ethylhexyl N,N-dimethylp-aminobenzoate, 2-phenylbenzimidazole-5-sulfonic acid, octocrylene, oxybenzone, homomenthyl salicylate, octyl salicylate, 4,4'-methoxy-tbutyldibenzoylmethane, 4-isopropyl dibenzoylmethane, 3-benzylidene camphor, 3-(4-methylbenzylidene) camphor, 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester of 4-(2-hydroxyethoxy)dibenzoylmethane, and mixtures thereof. Most preferred examples of actives useful herein include those selected from the group consisting of salicylic acid, cisretinoic acid, trans-retinoic acid, azelaic acid, erythromycin, resorcinol, ibuprofen, naproxen, hydrocortisone, phenoxyethanol, phenoxypropanol, phenoxyisopropanol, 2,4,4'-trichloro-2'-hydroxy diphenyl ether, 3,4,4'trichlorocarbanilide, 2-ethylhexyl p-methoxycinnamate, 2-ethylhexyl N,Ndimethyl-p-aminobenzoate, 2-phenylbenzimidazole-5-sulfonic acid,

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octocrylene, oxybenzone, homomenthyl salicylate, octyl salicylate, 4,4'-methoxy-t-butyldibenzoylmethane, 4-isopropyl dibenzoylmethane, 3-benzylidene camphor, 3-(4-methylbenzylidene) camphor, 4-N,N-(2-ethylhexyl)-methylaminobenzoic acid ester of 4-(2-hydroxyethoxy)dibenzoylmethane, and mixtures thereof. An especially preferred active useful herein is salicylic acid.

The compositions of the present invention are preferably in the form of a water-in-oil or an oil-in-water emulsion, most preferably in the form of an oil-in-water emulsion. These emulsions are typically used with water to cleanse the skin. Upon rinsing with water, these compositions are removed from the skin surface along with associated dirt, oils, bacteria, and other foreign material, and leave the antimicrobial active and other skin care actives on the skin.

The oil-in-water emulsions herein have desirable aesthetic properties, such as a rich and creamy, yet non-greasy, skin feel. These emulsions can span a broad range of consistencies from thin lotions to heavy creams. These emulsions typically have viscosities ranging from about 100 cps to about 500,000 cps, more preferably from about 1000 cps to about 150,000 cps, and most preferably from about 5000 cps to about 100,000 cps.

The emulsion compositions herein can span a wide range of pH values and can be acidic, basic, or neutral, depending on the particular active or actives employed. For example, for acidic actives, the pH of the composition should be carefully chosen so that it is at or below the pKa of the active. By standard definitions, the pKa value for a compound is that pH value at which the material is 50 percent dissociated or ionized to yield its conjugate base and a proton (or hydrated proton). Without being limited by theory, when the pH of the formulation is below the pKa of the active, it is belived that the active will exist primarily in its un-ionized form which should enhance its subsequent deposition onto the skin.

For example, salicylic acid has a reported pKa of 2.97 at 19<sup>o</sup>C in aqueous solution. Therefore, it would be useful to formulate salicylic acid containing compositions at or below a pH of about 2.97 in order to suppress ionization and maximize deposition from the emulsion. See CRC Handbook of Chemistry and Physics, 57th Edition, page D-150 (1976).

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For salicylic acid containing compositions the should be from about 2 to about 7, more preferably from about 2.5 to about 5, even more preferably from about 2.5 to about 4, and most preferably from about 2.5 to about 3.

Even though buffers can be utilized to help maintain the pH of the emulsion compositions, these are not required components, but are merely optional.

The compositions of the present invention comprise from about 0.1% to about 25%, preferably from about 0.1% to about 15%, and more preferably from about 6% to about 10% of an alkoxylated ether which is useful for solubilizing the active ingredients in the oil phase of oil-in-water emulsions. The alkoxylated ethers and diethers useful herein generally have a solubility in water of less than about 1 gram per about 100 grams of water at 25°C. These compounds are typically formulated into the oil phase of oil-in-water emulsions as described in the Examples below. Mixtures of alkoxylated ethers and diethers can be used herein. The alkoxylated ethers useful herein can be described by the following general formula:

wherein R is selected from the group consisting of H and  $C_1$ - $C_{30}$  straight chain or branched chain alkyl, m is an integer from 0 to about 6, R'is selected from the group consisting of methyl and ethyl, and n is an integer from about 3 to about 30.

Preferably R is selected from the group consisting of C<sub>2</sub>-C<sub>25</sub> straight chain or branched alkyl, m is an integer from 0 to about 2, R' is methyl, and n is an integer from about 5 to about 25. More preferably R is selected from the group consisting of C<sub>2</sub>-C<sub>20</sub> straight chain or branched chain alkyl, m is an integer from 0 to about 1, R' is methyl, and n is an integer from about 10 to about 20.

Nonlimiting examples of classes of alkoxylated ethers useful herein include propoxylated and butoxylated ethers of alcohols and polyols. These

compounds can be described as PPG and PBG alkyl ethers wherein the PPG and PBG are commonly used designations for polypropylene glycol and polybutylene glycol, respectively. The average number of PPG or PBG groups in these ethers is commonly given by a number designation after the PPG or PBG. For example, PPG-14 butyl ether, would designate a polypropylene glycol ether of butanol wherein the molecule has on average 14 propylene glycol units.

Nonlimiting examples of alkoxylated ethers useful herein include PPG-10 butyl ether, PPG-11 butyl ether, PPG-12 butyl ether, PPG-13 butyl ether, PPG-14 butyl ether, PPG-15 butyl ether, PPG-16 butyl ether, PPG-17 butyl ether, PPG-18 butyl ether, PPG-19 butyl ether, PPG-20 butyl ether, PPG-22 butyl ether, PPG-24 butyl ether, PPG-30 butyl ether, PPG-11 stearyl ether, PPG-15 stearyl ether, PPG-10 oleyl ether, PPG-7 lauryl ether, PPG-30 isocetyl ether, PPG-10 glyceryl ether, PPG-15 glyceryl ether, PPG-10 butyleneglycol ether, PPG-15 butylene glycol ether, PPG-27 glyceryl ether, PPG-30 cetyl ether, PPG-28 cetyl ether, PPG-10 cetyl ether, PPG-10 hexylene glycol ether, PPG-15 hexylene glycol ether, PPG-10 1,2,6-hexanetriol ether, PPG-15 1,2,6-hexanetriol ether, and mixtures thereof.

Preferred alkoxylated ethers are those selected from the group consisting of PPG-14 butyl ether, PPG-15 stearyl ether, PPG-11 stearyl ether, PPG-20 oleyl ether, and mixtures thereof.

More preferred alkoxylated ethers are those selected from the group consisting of PPG-14 butyl ether, PPG-15 stearyl ether, and mixtures thereof. PPG-14 butyl ether is available under the tradename Fluid AP from Union Carbide Corporation. PPG 15 stearyl ether is available under the tradename Arlamol E from ICI Americas Corporation.

Also useful herein are alkoxylated diethers. These compounds can be represented by the general formula:

$$H(OCH_2CH)_qO - CH_2 - CH_2 - CH_2 - O(CHCH_2O)_pH$$

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wherein each R" is selected from the group consisting of methyl and ethyl, p is an integer from about 1 to about 6, and each q and r are independently selected so that their sum is an integer from about 3 to about 30. Preferably R" is methyl, p is an integer from about 2 to about 4, and each q and r are independently selected so that their sum is an integer from about 5 to about 25. More preferably R" is methyl, p is an integer from 2 to about 4, and each q and r are independently selected so that their sum is an integer from about 10 to about 20.

Nonlimiting examples of alkoxylated diethers useful herein include those selected from the group consisting of PPG-10 1,4-butanediol diether, PPG-12 1,4-butanediol diether, PPG-14 1,4-butanediol diether, PPG-2 butanediol diether, PPG-10 1,6-hexanediol diether, PPG-12 1,6-hexanediol diether, PPG-14 hexanediol diether, PPG-20 hexanediol diether, and mixtures thereof. Preferred are those selected from the group consisting of PPG-10 1,4-butanediol diether, PPG-12 1,4-butanediol diether, PPG-10 1,6-hexandiol diether, and PPG-12 hexanediol diether, and mixtures thereof. More preferred is PPG-10 1,4-butanediol diether. This compound is commercially available under the tradename Macol 57 from PPG/Mazer Corporation.

Also preferred for use in the compositions herein is a deposition aiding polymer for increasing the deposition of the antimicrobial agent and/or any skin care active present in the composition. The compositions of the present invention preferably comprise from 0% to about 10%, more preferably from about 0.1% to about 10%, even more preferably from about 0.25% to about 7.5%, and most preferably from about 0.50% to about 5% of a deposition aiding polymer for increasing the deposition of the skin care active ingredient upon the skin. Without being limited by theory, the deposition aiding polymer is believed to aid in the deposition of the active ingredient from the oil phase of the oil-in-water emulsion, thereby depositing the active onto the skin during the cleansing process and helping the active to adhere to the skin during the rinsing process. The deposition aiding polymers useful herein are typically formulated into the oil phase of the oil-in-water emulsions as described in the Examples below.

A variety of deposition aiding polymers are useful herein and include those selected from the group consisting of hydroxy-terminated urethane polymers, polypropylene glycols, and mixtures thereof.

When a combination of a hydroxy-terminated urethane polymer and a polypropylene glycol polymer is used as the deposition aiding polymer, the weight/weight ratio of the hydroxy-terminated urethane polymer to the polypropylene glycol polymer is from about 1:1.5 to about 1.5:1, preferably from about 1:25:1 to about 1:1.25, more preferably from about 1:1.1 to about 1:1.1, and most preferably about 1:1.

Hydroxy-terminated Urethane Polymers The hydroxy-terminated urethane polymers useful as deposition aids herein are those generally described in U.S. Patent 5,051,260, to Chess et al., issued September 24, 1991; U.S. Patent No. 5,045,317, to Chess et al. issued September 3, 1991; and U.S. Patent No. 4,971,800, to Chess et al., issued November 20, 1990; all of which are incorporated by reference herein in their entirety.

These hydroxy-terminated urethane compounds are represented by the general formula (it is to be understood that this formula represents a linear polymer chain

wherein R represents an alkyl or alkenyl radical having from about one to about 20 carbon atoms, or a cycloalkyl or cycloalkyneyl radical containing form about 5 to about 10 carbon atoms, or a mononuclear or fused ring aryl radical containing from about 6 to about 10 carbon atoms,

unsbustituted or substituted with one or more C1-C6 alkyl, C1-C6 alkoxy, C1-C6 alkoxy-substituted C1-C6, nitro or amino groups or halogen atoms; R is the same or different alkyl or akenyl radical; m is an integer selected so as to provide an (O-R) moiety having a molecular weight of from about 40 to about 6000, preferably from about 400 to about 2000; and n and n' are the same or different integers of from 0 to about 30 inclusive, correlated with m so as to provide a hydroxy-terminated urethane compound having a molecular weight of up to about 200,000, preferably from about 220 to about 37,000, and more preferably from about 1000 to about 5000.

The hydroxy-terminated urethane compounds are prepared using standard synthetic techniques from the reaction of linear alkylene or polyalkylene glycols or polyethers with monomeric organic diisocyanates. The linear alkylene or polyalkylene glycols or polyethers are represented by the general formula:

H-(O-R<sup>1</sup>) O-H wherein R and m are as described in the preceding paragraph. Specific nonlimiting examples of polyalkylene glycol or polyether reactants include: diethylene glycol, triethylene glycol, PEG-4, PEG-6, PEG-8, PEG-9, PEG-10, PEG-12, PEG-14, PEG-16, PEG-18, PEG-20, PEG-32, PEG-40, PPG-9, PPG-12, PPG-15, PPG-17, PPG-20, PPG-26, PPG-30, PPG-34, and polytetramethylene glycols having molecular weights ranging from about 600 to 6000, and the like. The terms "PEG" and "PPG" are commonly used CTFA designations for polyethylene glycol and polypropylene glycol, respectively. The number following the designation indicates the average number of units of ethylene glycol or propylene glycol in the molecule. Also, mixtures of polyalkylene glycols or polyethers described hereinabove can also be employed in preparing the hydroxy-terminated urethanes useful herein. The monomeric organic diisocyanates are represented by the general formula:

$$O=C=N-R-N=C=O$$

wherein R is an alkyl or alkenyl radical having from about one to about 20 carbon atoms, or a cycloalkyl or cycloalkyneyl radical containing form about 5 to about 10 carbon atoms, or a mononuclear or fused ring aryl radical containing from about 6 to about 10 carbon atoms, unsbustituted or substituted with one or more C1-C6 alkyl, C1-C6 alkoxy, C1-C6 alkoxy-substituted C1-C6, nitro or amino groups or halogen atoms. Nonlimiting

examples of diisocyanates are aromatic diisocyanates, such as mphenylenediisocyanate, p-phenylenediisocyanate, 4-t-butyl-mphenylenediisocyanate, 4-methoxy-m-phenylenediisocyanate, 4-phenoxym-phenylenediisocyanate, 4-chloro-m-phenylenediisocyanate, toluenediisocyanates (either as a mixture of isomers, e.g., the commercially available mixture of 80% 2,4-toluenediisocyanate and 20% 2,6-toluenediisocyanate, or as the individual isomers themselves), mxylylenediisocyanate, p-xylylendiisocyanate, cumene-2,4-diisocyanate, durenediisocyanate, 1,4-naphthylenediisocyanate, 1,5naphthylenediisocyanate, 1,8-naphthylenediisocyanate, 2,6naphthylenediisocyanate, 1,5-tetrahydronophthylenediisocyanate, p,p'diphenyldiisocyanate, diphenylmethane-4,4'-diisocyanate, 2,4diphenylhexane-1,6-diisocyanate, "bitolylenediisocyanate" (3,3'-dimethyl-4,4'-biphenylenediisocyanate), "dianisidinediisocyanate" (3,3'-dimethoxy-4,4'-biphenylenediisocyanate); aliphatic diisocyanates, such as methylenediisocyanates, ethylenediisocyanate, the tri-, tetra-, penta-, hexa-, octa-, nona- and decamethylene-omega,omega-diisocyanates, 2-chlorotrimethylenediisocyanate, 2,3-dimethyltetramethylenediisocyante, and the like, as well as mixtures thereof.

A preferred hydroxy-terminated urethane polymer useful herein is poly[oxy(methyl-1,2-ethanediyl)],alpha-hydro-omega-hydroxy-, polymer with 1,1'methylene-bis-(4-isocyanatocyclohexane). This material is also known by the CTFA designation polyolprepolymer-2 and is commercially available as Topicare 35A from Penederm Inc. through its distributor Barnet Products Corp. (Englewood Cliffs, NJ).

<u>Polypropylene Glycols</u> Polypropylene glycols are useful as deposition aiding polymers herein. Polypropylene glycols are polymers which are typically formed from the polymerization of propylene oxide, propylene glycol, propylchlorohydrin, propylbromohydrin, and other related materials. Polypropylene glycols are represented by the following formula.



wherein n is an integer from about 10 to about 50, preferably wherein n is an integer from about 15 to about 40, and more preferably wherein n is an

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integer from about 20 to about 34. In the above structure, even though one isomeric orientation is depicted for convenience, this depiction is not intended to preclude other isomeric structures. The polypropylene glycols are commonly designated as PPG's followed by a number indicating the average number of repeating units in the structure. For example, PPG-30 would correspond to the above structure wherein n has an average value of about 30. Based on this nomenclature, the polypropylene glycols useful herein encompass those designated as PPG-10 through PPG-50, more preferably those designated as PPG-15 through PPG-40, and most preferably those designated as PPG-20 through PPG-34. An especially preferred PPG for use in the compositions herein is PPG-30, which is sold under the tradename Polyglycol P-4000 and is commercially available from Dow Chemical Corporation.

The compositions of the present invention comprise from 0% to about 10%, preferably from about 0.5% to about 5%, and more preferably from about 1% to about 4% of a polymeric thickener. A wide variety of thickeners can be employed herein with the choice depending upon the pH of the formulation and other emulsion components chosen. For compositions having a pH from about 2 to about 7, the thickeners should be stable within that pH range, i.e. they should not degrade and should not lose their thickening ability.

Preferred thickeners include those selected from the group consisting of crosslinked polyacrylate polymers, alkyl modified hydroxyalkylcellulose polymers, quaternary ammonium hydroxalkyl celluose polymers, and mixtures thereof.

#### Crosslinked Polyacrylate Polymers

The crosslinked polyacrylate polymers useful as thickeners include both cationic and nonionic polymers, with the cationics being generally preferred.

Examples of useful crosslinked nonionic polyacrylate polymers and crosslinked cationic polyacrylate polymers are those described in U.S. Patent 5,100,660, to Hawe et al., issued March 31, 1992; U.S. Patent

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4,849,484, to Heard, issued July 18, 1989; U.S. Patent 4,835,206, to Farrar et al., issued May 30, 1989; U.S. Patent 4,628,078 to Glover et al. issued December 9, 1986; U.S. Patent 4,599,379 to Flesher et al. issued July 8, 1986; and EP 228,868, to Farrar et al., published July 15, 1987; all of which are incorporated by reference herein in their entirety.

The crosslinked polyacrylate polymers are high molecular weight materials that can be characterized by the general formula: (A) (B) (C) and comprise the monomer units (A), (B), and (C), wherein (A) is a dialkylaminoalkyl acrylate monomer or its quaternary ammonium or acid addition salt, (B) is a dialkylaminoalkyl methacrylate monomer or its quaternary ammonium or acid addition salt, (C) is a monomer that is polymerizable with (A) or (B), for example a monomer having a carbon-carbon double bond or other such polymerizable functional group, 1 is an integer of 0 or greater, m is an integer of 0 or greater, n is an integer of 0 or greater.

The (C) monomer can be selected from any of the commonly used monomers. Nonlimiting examples of these monomers include ethylene, propylene, butylene, isobutylene, eicosene, maleic anhydride, acrylamide, methacrylamide, maleic acid, acrolein, cyclohexene, ethyl vinyl ether, and methyl vinyl ether. In the cationic polymers of the present invention, (C) is preferably acrylamide. The alkyl portions of the (A) and (B) monomers are short chain length alkyls such as  $C_1 - C_8$ , preferably  $C_1 - C_5$ , more preferably  $C_1 - C_3$ , and most preferably  $C_1 - C_2$ . When quaternzied, the polymers are preferably quaternized with short chain alkyls, i.e.,  $C_1 - C_8$ , preferably  $C_1 - C_5$ , more preferably  $C_1 - C_3$ , and most preferably  $C_1 - C_2$ . The acid addition salts refer to polymers having protonated amino groups. Acid addition salts can be performed through the use of halogen (e.g. chloride), acetic, phosphoric, nitric, citric, or other acids.

These (A) (B) (C) polymers also comprise a crosslinking agent, which is most typically a material containing two or more unsaturated functional groups. The crosslinking agent is reacted with the monomer units of the polymer and is incorporated into the polymer thereby forming links or covalent bonds between two or more individual polymer chains or between two or more sections of the same polymer chain. Nonlimiting examples of suitable crosslinking agents include those selected from the group

consisting of methylenebisacrylamides, diallyldialkyl ammonium halides, polyalkenyl polyethers of polyhydric alcohols, allyl acrylates, vinyloxyalkylacrylates, and polyfunctional vinylidenes. Specific examples of crosslinking agents useful herein include those selected from the group consisting of methylenebisacrylamide, ethylene glycol di-(meth)acrylate, di-(meth)acrylamide, cyanomethylacrylate, vinyloxyethylacrylate, vinyloxyethylmethacrylate, allyl pentaerythritol, trimethylolpropane diallylether, allyl sucrose, butadiene, isoprene, divinyl benzene, divinyl naphthalene, ethyl vinyl ether, methyl vinyl ether, and allyl acrylate. Other crosslinkers include formaldehyde and glyoxal. Preferred for use herein as a crosslinking agent is methylenebisacrylamide.

Widely varying amounts of the crosslinking agent can be employed depending upon the properties desired in the final polymer, e.g. viscosifying effect. Without being limited by theory, it is believed that incorporation of a crosslinking agent into these cationic polymers provides a material that is a more effective viscosifying agent without negatives such as stringiness and viscosity breakdown in the presence of electrolytes. The crosslinking agent, when present, can comprise from about 1 ppm to about 1000 ppm, preferably from about 5 ppm to about 750 ppm, more preferably from about 25 ppm to about 500 ppm, even more preferably from about 100 ppm to about 500 ppm, and most preferably from about 250 ppm to about 500 ppm of the total weight of the polymer on a weight/weight basis.

The intrinsic viscosity of the crosslinked polymer, measured in one molar sodium chloride solution at 25°C, is generally above 6, preferably from about 8 to about 14. The molecular weight (weight average) of the crosslinked polymers hereof is high, and is believed to typically be between about 1 million and about 30 million. The specific molecular weight is not critical and lower or higher weight average molecular weights can be used as long as the polymer retains its intended viscosifying effects in water or other aqueous carriers of the compositions hereof. Preferably, a 1.0% solution of the polymer (on an actives basis) in deionized water will have a viscosity at 25°C of at least about 20,000 cP, preferably at least about 30,000 cP, when measured at 20 RPM by a Brookfield RVT (Brookfield Engineering Laboratories, Inc. Stoughton, MA, USA).

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These cationic polymers can be made by polymerization of an aqueous solution containing from about 20% to about 60%, generally from about 25% to about 40%, by weight monomer, in the presence of an initiator (usually redox or thermal) until the polymerization terminates. The crosslinking agent can also be added to the solution of the monomers to be polymerized, to incorporate it into the polymer. In the polymerization reactions, the temperature generally starts between about O and 95°C. The polymerization can be conducted by forming a reverse phase dispersion of an aqueous phase of the monomers (and also any additional crosslinking agents) into a nonaqueous liquid, e.g. mineral oil, lanolin, isododecane, oleyl alcohol, and other volatile and nonvolatile esters, ethers, and alcohols, and the like.

All percentages describing the polymer in this section of the description herein are molar, unless otherwise specified. When the polymer contains (C) monomer, the molar proportion of (C) monomer, based on the total molar amount of (A), (B), and (C), can be from 0% to about 99%. The molar proportions of (A) and (B) can each be from 0% to 100%. When acrylamide, is used as the (C) monomer, it will preferably be used at a level of from about 20% to about 99%, more preferably from about 50% to about 90%.

Where monomer (A) and (B) are both present, the ratio of monomer (A) to monomer (B) in the final polymer, on a molar basis, is preferably from about 99:5 to about 15:85, more preferably from about 80:20 to about 20:80. Alternatively, in another class of polymers, the ratio is from about 5:95 to about 50:50, preferably from about 5:95 to about 25:75.

In another alternative class of polymers, the ratio (A):(B) is from about 50:50 to about 85:15. Preferably the ratio (A):(B) is about 60:40 to about 85:15, most preferably about 75:25 to about 85:15.

Most preferred is where monomer (A) is not present and the ratio of monomer (B):monomer (C) is from about 30:70 to about 70:30, preferably from about 40:60 to about 60:40 and most preferably from about 45:55 to about 55:45.

Cationic polymers that are useful herein that are especially preferred are those conforming to the general structure (A) (B) (C) wherein I is zero, (B) is methyl quaternized dimethylaminoethyl methacrylate, the ratio of (B):(C) is from about 45:55 to about 55:45, and the crosslinking agent is methylenebisacrylamide. An example of such a cationic polymer is one that is commercially available as a mineral oil dispersion (which can also include various dispersing aids such as PPG-1 trideceth-6) under the trademark Salcare SC92 from Allied Colloids Ltd. (Norfolk, Virginia). This polymer has the proposed CTFA designation, "Polyquaternium 32 (and) Mineral Oil".

Other cationic polymers useful herein, are those not containing acrylamide or other (C) monomers, that is, n is zero. In these polymers the (A) and (B) monomer components are as described above. An especially preferred group of these non-acrylamide containing polymers is one in which I is also zero. In this instance the polymer is essentially a homopolymer of a dialkylaminoalkyl methacrlyate monomer or its quaternary ammonium or acid addition salt. These diaklylaminoalkyl methacrylate polymers preferably contain a crosslinking agent as described above.

A cationic polymer, which is essentially a homopolymer, useful herein is one conforming to the general structure (A)<sub>1</sub>(B)<sub>m</sub>(C)<sub>m</sub> wherein I is zero, (B) is methyl quaternized dimethylaminoethyl methacrylate, n is zero, and the crosslinking agent is methylenebisacrylamide. An example of such a homopolymer is commercially available as a mixture containing approximately 50% of the polymer, approximately 44% mineral oil, and approximately 6% PPG-1 trideceth-6 as a dispersing aid, from Allied Colloids Ltd, (Norfolk, VA) under the trademark Salcare SC95. This polymer has recently been given the CTFA designation "Polyquaternium 37 (and) Mineral Oil (and) PPG-1 Trideceth-6".

#### Alkyl Hydroxyalkylcellulose Ethers

By the term "alkyl hydroxyalkylcellulose ethers" as used herein is meant polymers containing a cellulose backbone, i.e. a polysaccharaide backbone of repeating glucose units. In these polymers, the hydroxy groups of the cellulose polymer are hydroxyalkylated (prefereably hydroxyethylated or hydropropylated) to form a hydroxyalkylated cellulose

which is then further modified with a C10-C30 straight chain or branched chain alkyl group through an ether linkage. Typically these polymers are ethers of C10-C30 straight or branched chain alcohols with hydroxyalkylcelluloses. Examples of alkyl groups useful herein include those selected from the group consisting of stearyl, isostearyl, lauryl, myristyl, cetyl, isocetyl, cocoyl (i.e. alkyl groups derived from the alcohols of coconut oil), palmityl, oleyl, linoleyl, linolenyl, rincioleyl, behenyl, and mixtures thereof.

Preferred among the alkyl hydroxyalkyl cellulose ethers is the material given the CTFA designation cetyl hydroxyethylcellulose, which is the ether of cetyl alcohol and hydroxyethylcellulose. This material is sold under the tradename Natrosol CS Plus from Aqualon Corporation.

#### Ouaternary Ammonium Hydroxyalkylcellulose Polymers

By the term "quaternary ammonium hydroyxalkylcellulose polymer" as used herein is meant polymers containing a cellulose backbone, i.e. a polysaccharaide backbone of repeating glucose units. In these polymers, the hydroxy groups of the cellulose polymer are hydroxyalkylated (preferably hydroxyethylated or hydroxypropylated) to form a hydroxyalkylated cellulose which is then further modified with a cationic quaternary ammonium or protonated ammonium group.

Preferred cationic modifying groups are those having at least one C10-20 alkyl chain and two shorter alkyl chains (i.e. C1 or C2) on the nitrogen. The substituent on the cellulose polymer can thus be depicted as - (X)NRR'R" wherein X is hydroxyalkyl (preferably -OCH<sub>2</sub>CH<sub>2</sub> - or - OCH<sub>2</sub>CHOHCH<sub>2</sub>-), R and R' are methyl or ethyl, and R" is C10-20 alkyl [preferably lauryl, stearyl, or cocoyl (i.e. a mixture of alkyl groups derived from coconut oil)]. It has alternatively been found that when R, R', and R" are all methyl (i.e. the trimonium group) that useful cellulose polymers are also obtained.

In other alternatives structures, the substituent on the cellulose polymer can be depicted as -(X)-OCH<sub>2</sub>CH<sub>2</sub>-NRR'R" wherein X is hydroxyalkyl (preferably -OCH<sub>2</sub>CH<sub>2</sub>- or -OCH<sub>2</sub>CHOHCH<sub>2</sub>-), R and R' are methyl or ethyl, and R" is C10-20 alkyl [preferably lauryl, stearyl, or cocoyl (i.e. a

mixture of alkyl groups derived from coconut oil)]. It has alternatively been found that when R, R', and R" are all methyl (i.e. the trimonium group) that useful cellulose polymers are also obtained.

In yet other alternative structures the cationic substituent on the cellulose contains both a hydroxyethyl and a hydroxypropyl group such that the moiety can be depicted as -(OCH\_CH\_O)-CH\_CHOHCH\_NRR'R" wherein R, R', and R" are methyl or ethyl, and R" is C10-20 alkyl [preferably lauryl, stearyl, or cocoyl (i.e. a mixture of alkyl groups derived from coconut oil)], or alternatively wherein R, R', and R" are all methyl (i.e. the trimonium group).

Commercially available cationic modified celluloses include: CTFA designated polyquaternium-24, which is the quaternary ammonium salt of hydroxyethyl cellulose reacted with a lauryl dimethyl ammonium substituted epoxide (wherein in the above formula -(X)-OCH<sub>2</sub>CH<sub>2</sub>-NRR'R", X is -OCH<sub>2</sub>CH<sub>2</sub>-, R and R' are methyl, and R" is stearyl). This material is sold under the tradename Quatrisoft Polymer LM-200 and is available from Amerchol Corporation.

Other commericially available cationic modified celluloses inloude: laurdimonium hydroxethyl cellulose (wherein in the above formula - (X)NRR'R", X is -OCH<sub>2</sub>CH<sub>2</sub>-, R and R' are methyl, and R" is lauryl), steardimonium hydroxyethyl cellulose (wherein in the above formula - (X)NRR'R", X is -OCH<sub>2</sub>CH<sub>2</sub>-, R and R' are methyl, and R" is stearyl), and cocodimonium hydroxyethyl cellulose (wherein in the above formula - (X)NRR'R", X is -OCH<sub>2</sub>CH<sub>2</sub>-, R and R' are methyl, and R" is cocoyl). These three materials are known by the trade names Crodacel QL, Crodacel QS, and Crodacel QM, respectively, which are all commercially available from Croda Corp. Another highly useful cationic cellulose is laurdimmonium hydroxypropyl oxyethyl cellulose (wherein the modifying group on the cellulose is -(OCH<sub>2</sub>CH<sub>2</sub>O)-CH<sub>2</sub>CHOHCH<sub>2</sub>NRR'R", wherein R R' are methyl and R" is lauryl), which is commercially available as Crodacel QL Special, from Croda Corp.

Preferred among the quaternary ammonium hydroalkyl cellulose polymers is polyquaternium-24.

The compositions of the present invention comprise from about 25% to about 99.7%, more preferably from about 65% to about 95%, and most preferably from about 70% to about 90% water.

Other suitable optional components for use in the compositions herein are:

#### Fatty Acids

An optional component of the present invention is a fatty acid. These fatty acids can be used to increase emulsion viscosity and to provide a smooth feel to the finished emulsion. When used herein, these fatty acids can comprise from about 0.1% to about 10%, more preferably from about 0.1% to about 7.5%, and most preferably from about 0.1% to about 5% of the compositions.

By the term "fatty acid" is meant any organic acid from natural or synthetic sources having from about 10 to about 40 carbon atoms, more preferably from about 10 to about 30 carbon atoms, and most preferably from about 12 to about 22 carbon atoms. Also included within this definition of fatty acid are the corresponding branched carbon chain materials.

Nonlimiting examples of fatty alcohols include those selected from the group consisting of lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, oleic acid, linoleic acid, linolenic acid, ricinoleic acid, behenic acid, isostearic acid, and mixtures thereof. Examples of fatty alcohols are described in <a href="https://examples.org/ref">CTFA International Cosmetic Ingredient</a>
Dictionary Fourth Edition, which is incorporated herein by reference in its entirety.

Also useful are hydroxy substituted derivatives of the fatty acids described herein. Nonlimiting examples of these materials include hydroxystearic acid, hydroxypalmitic acid, hydroxylauric acid, and mixtures thereof.

#### Fatty Alcohols

An optional component of the present invention is a fatty alcohol. These fatty alochols can be used to increase emulsion viscosity and to provide a

smooth feel to the finished emulsion. When used herein, these fatty alcohols can comprise from about 0.1% to about 10%, more preferably from about 0.1% to about 7.5%, and most preferably from about 0.1% to about 5% of the compositions.

By the term "fatty alcohol" is meant any organic alcohol from natural or synthetic sources having from about 10 to about 40 carbon atoms, more preferably from about 10 to about 30 carbon atoms, and most preferably from about 12 to about 22 carbon atoms. Also included within this definition of fatty alcohol are the corresponding branched carbon chain materials.

Nonlimiting examples of fatty alcohols include those selected from the group consisting of lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, linoleyl alcohol, linoleyl alcohol, ricinoleyl alcohol, behenyl alcohol, and mixtures thereof. Examples of fatty alcohols are described in <a href="CTFA International Cosmetic Ingredient Dictionary">CTFA International Cosmetic Ingredient Dictionary</a> Fourth Edition, which is incorporated herein by reference in its entirety.

#### **Humectants**

Another optional component of the compositions of the present invention is a humectant. When used herein, the humectant can comprise from about 0.1% to about 20%, more preferably from about 0.5% to about 10%, and most preferably from about 1% to about 5% of the compositions. Even though these materials are defined herein as humectants, they can also possess moisturizing, skin conditioning, and other related properties.

Examples of humectants useful herein include materials such as urea; guanidine; glycolic acid and glycolate salts (e.g. ammonium and quaternary alkyl ammonium); lactic acid and lactate salts (e.g. ammonium and quaternary alkyl ammonium); aloe vera in any of its variety of forms (e.g., aloe vera gel); polyhydroxy alcohols such as sorbitol, glycerol, low molecular weight polypropylene glycols (e.g., dipropylene glycol and tripropylene glycol), hexanetriol, propylene glycol, butylene glycol, hexylene glycol, and the like; polyethylene glycol; sugars and starches; sugar and starch derivatives (e.g., alkoxylated glucose); hyaluronic acid;

chitin, starch-grafted sodium polyacrylates such as Sanwet (RTM) IM-1000, IM-1500, and IM-2500 (available from Celanese Superabsorbent Materials, Portsmouth, VA); lactamide monoethanolamine; acetamide monoethanolamine; propoxylated glycerol (as described in U.S. Patent No. 4,976,953 to Orr et al., issued December 11,1990, which is incorporated by reference herein in its entirety); and mixtures thereof.

Preferred humectants useful in the compositions of the present invention are urea, C3-C6 diols and triols, low molecular weight polypropylene glycols, and propoxylated glycerin. Preferred humectants include those materials selected from the group consisting of urea, propylene glycol, 1,3-dihydroxypropane, glycerin, butylene glycol, hexylene glycol, 1,4-dihydroxyhexane, 1,2,6-hexanetriol, dipropylene glycol, tripropylene glycol, and mixtures thereof. More preferred are those selected from the group consisting of urea, glycerin, butylene glycol, hexylene glycol, glycerin, dipropylene glycol, tripropylene glycol, and mixtures thereof. Most preferred is urea, glycerin, and mixtures thereof.

#### **Emollients**

The compositions of the present invention can also include an emollient. Examples of suitable emollients include, but are not limited to, volatile and non-volatile silicone oils (e.g., dimethicone, cyclomethicone, dimethiconol, and the like), highly branched hydrocarbons, and non-polar carboxylic acid and alcohol esters, and mixtures thereof. Emollients useful in the instant invention are further described in U.S. Patent No. 4,919,934, to Deckner et al., issued April 24 1990, which is incorporated herein by reference in its entirety.

The emollients can typically comprise in total from about 0.5% to about 50%, more preferably from about 0.5% to about 25%, and most preferably from about 0.5% to about 15% by weight of the compositions of the present invention.

#### Additional Ingredients

A variety of additional ingredients can be incorporated into the compositions of the present invention. Non-limiting examples of these

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additional ingredients include vitamins and derivatives thereof (e.g. tocopherol, tocopherol acetate, and the like); other thickening agents (e.g., polyacrylamide and C isoparaffin and laureth-7, available as Sepigel 305 from Seppic Corp., Fairfield; NJ; and branched polysaccharides such as scleroglucan available under the tradename Clearogel CS 11 from Michel Mercier Products Inc., Mountainside, NJ); acrylic acid homopolymers crosslinked with an allyl ether of pentaerythritol or an allyl ether of sucrose which are known by the CTFA designation of carbomer and are commercially available from B.F. Goodrich under the Carbopol trademark; and copolymers of C10-30 alkyl acrylates with acrylic acid, alkyl esters of acrylic acid, methacrylic acid, alkyl esters of methacrylic acid, crosslinked with an allyl ether of sucrose or an allyl ether of pentaerythritol, which are known by the CTFA designation acrylates/C10-30 alkyl acrylate crosspolymer, and are commericially available as Carbopol 1342, Pemulen TR-1, and Pemulen TR-2, from B.F. Goodrich); resins; gums (e.g. guar gum, xanthan gum and the like); waxes (both naturally occurring and synthetic); polymers for aiding the film-forming properties and substantivity of the composition (such as a copolymer of eicosene and vinyl pyrrolidone, an example of which is available from GAF Chemical Corporation as Ganex V-220<sup>r</sup>); abrasive scrub particles for cleansing and exfoliating the skin [e.g., ACuscrub Mild Abrasives (e.g., ACuscrub 30, 31, 32, 40, 41, 42, 43, 44, 50, 51, and 52) available from Allied Signal, Inc., Morristown, NJ; and 3M Brand PMU Capsules microecapsulated mineral oil available from 3M Corporation, St. Paul, MN]; preservatives for maintaining the antimicrobial integrity of the compositions; skin penetration aids such as DMSO, 1dodecylazacycloheptan-2-one (available as Azone from the Upjohn Co.) and the like; artificial tanning ingredients and tan accelerators such as dihydroxyacetone, tyrosine, tyrosine esters such as ethyl tyrosinate, and phospho-DOPA); skin bleaching (or lightening) agents including but not limited to hydroquinone, kojic acid and sodium metabisulfite; antioxidants; chelators and sequestrants; and aesthetic components such as fragrances, pigments, colorings, essential oils, skin sensates, astringents, skin soothing agents, skin healing agents and the like, nonlimiting examples of these aesthetic components include panthenol and derivatives (e.g. ethyl panthenol), aloe vera, pantothenic acid and its derivatives, clove oil,

menthol, camphor, eucalyptus oil, eugenol, menthyl lactate, witch hazel distillate, allantoin, bisabalol, dipotassium glycyrrhizinate and the like.

## Methods for Cleansing the Skin and Depositing an Active Upon the Skin Surface

The compositions of the present invention are useful for cleansing the skin and also for depositing an antimicrobial agent onto the skin. Typically, a suitable amount of the cleansing composition is applied to the skin to be cleansed. It is preferred to premoisten the skin with water. Alternatively, a suitable amount of the cleansing composition can be applied to the skin via intermediate application to a washcloth, a sponge, or other application device. It has been found that the compositions of the present invention provide their optimal cleansing performance when combined with water during the cleansing process. To complete the cleansing process, the composition is thoroughly rinsed from the skin with water, leaving the antimicrobial agent on the skin surface. To cleanse the skin and deposit an active, an effective amount of the emulsion composition is utilized, for example, from about 0.5 mg/cm<sup>2</sup> to about 5.0 mg/cm<sup>2</sup> of skin area to be cleansed.

The following examples illustrate compositions of the present invention.

#### EXAMPLES I-V

Ingredient	I/%	II/%	III/%	IV/%	V/%	
Water	to 100					
PPG-15 Stearyl Ether	4.0	5.0	3.5	4.5	5.5	
Glycerin	3.0	3.5	2.8	3.2	3.0	
Salicylic Acid	2.0	1.0	2.0	1.5	2.0	
Distearyl Dimethyl	1.5	1.0	0.5	1.0	1.5	
Ammonium Chloride						
Cetyl Alcohol	0.8	1.5	1.0	0.5	2.0	
Steareth-21	0.5	0.5	0.6	0.4	0.5	
Behenyl Alcohol	0.3	0.5	1.0	0.8	0.4	
PPG-30	0.25	0.25	0.3	0.25	0.25	
Steareth-2	0.25	0.3	0.3	0.2	0.25	

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Perfume	0.2	0.25	0.2	0.35	0.3
Disodium EDTA	0.01	0.01	0.01	0.01	0.01
Cetyl betaine	2.0	3.0	2.0	2.5	3.5
Sodium Lauryl	1.0	1.5	1.0	1.2	1.7
Sulphate					1.7
Menthol	0.075	0	0	0	0.08
JMAC TD1	0.01	0.01	0.02	0.005	0.08
Polyethylene Beads <sup>2</sup>	0	0	1.0	1.0	1.0

- 1. Supplied by Johnson Matthey
- 2. Available as Acuscrub 51 Mild Abrasive from Allied Signal, Inc.

The compositions of the examples can be prepared as follows:

The glycerin, disodium EDTA and water are mixed in a first vessel. The mixture is heated to 75-80 OC. The PPG-15 stearyl ether, salicylic acid and the PPG-30 are mixed together in a second vessel and the resulting mixture is heated to 75-80 °C. When the oil phase has reached 55 °C the stearyl alcohol, cetyl alcohol, behenyl alcohol, distearyldimonium chloride, steareth-21 and steareth-2 are added to the oil phase. Mixing of the oil phase is continued whilst heating to 75-80 °C. When both phases have reached 75-80 °C, the oil phase is transferred from the second vessel to the first vessel with mixing. The main batch is then emulsified whilst maintaining a temperature of 75-80 <sup>O</sup>C. The mixture is then cooled to 45 <sup>0</sup>C, and the perfume and menthol are added. The mixture is cooled further. In a third vessel the cetyl betaine and the polyethylene beads are mixed until the beads are dispersed. The sodium lauryl sulphate is then added to the third vessel and mixing is continued for 30 minutes. When the main batch has reached a temperature of 35 °C, the surfactant premix is transferred from the third vessel to the main batch. The JMAC TD is then added to the main batch. The resulting batch is mixed for at least an hour while cooling to 29-31 <sup>OC</sup>. The batch is then ready for packing.

The resulting emulsions are useful for application to the skin for cleansing and antibacterial purposes and for treating acne.

#### **CLAIMS:**

- 1. A cleansing composition comprising:
  - (a) from about 0.1% to about 30% by weight of an emulsifier selected from amphoteric, zwitterionic, nonionic, anionic and cationic emulsifiers and mixtures thereof;
  - (b) from about 0.00001% to about 5% of an antimicrobial agent, wherein the antimicrobial agent comprises a silver compound deposited on a particulate inert support material; and;
  - (c) water.
- 2. A composition according to Claim 1 wherein the silver compound is present in an amount of from about 0.5% to about 75%, preferably from about 0.5% to about 50%, more preferably from about 5% to about 30% by weight of the antimicrobial agent.
- 3. A composition according to Claim 1 or 2 wherein the particulate support material has an average particle size of less than about 25 micrometres.
- 4. A composition according to any of Claims 1 to 3 wherein the particulate support material has an average particle size of from about 0.01 micrometres to about 15 micrometres.
- 5. A composition according to any of Claims 1 to 4 wherein the particulate inert support material is selected from oxides of titanium, magnesium, aluminium, silicon, cerium, zirconium, hafnium, niobium and tantalum, calcium hydroxyapatite and barium sulphate.

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6. A composition according to any of Claims 1 to 5 wherein the support material is titanium dioxide.

- 7. A composition according to Claim 6 wherein the titanium dioxide is selected from anatase titanium dioxide, rutile titanium dioxide and brookite titanium dioxide, and mixtures thereof.
- 8. A composition according to Claim 6 or 7 wherein the titanium dioxide has a primary crystal size of from about 0.005 micrometres to about 5 micrometres.
- 9. A composition according to Claim 8 wherein the titanium dioxide has a primary crystal size of from about 0.01 to about 1 micrometre.
- A composition according to any of Claims 1 to 9 wherein the particulate support material has a mean surface area of from about 1 to about 300 m<sup>2</sup>/g.
- 11. A composition according to any of Claims 1 to 10 wherein the silver compound is selected from AgCl, AgBr, Ag2CO<sub>3</sub>, AgOH and Ag<sub>3</sub>PO<sub>4</sub>.
- 12. A composition according to any of Claims 1 to 11 wherein the silver compound is AgCl.
- 13. A composition according to any of Claims 1 to 12 comprising from about 0.0001% to about 3%, preferably from about 0.0001% to about 1%, more preferably from about 0.0001% to about 0.1% by weight of the antimicrobial agent.
- 14. A composition according to any of Claims 1 to 13 comprising from about 0.1% to about 20%, preferably from about 1% to about 15% by weight of the emulsifier.
- 15. A composition according to any of Claims 1 to 14 wherein the composition is in the form of an oil-in-water emulsion.
- 16. A composition according to any of Claims 1 to 15 additionally comprising from about 0.01% to about 10% by weight of skin care active.

- 17. A composition according to Claim 16 wherein the skin care active is selected from salicylic acid, azelaic acid and retinoic acid and mixtures thereof.
- 18. A composition according to Claim 16 or 17 wherein the acidic skin care active is salicylic acid.

<u>:</u>

#### INTERNATIONAL SEARCH REPORT

International application No. PCT/US96/20067

		FC1/0390/2006/
IPC(6) US CL	ASSIFICATION OF SUBJECT MATTER :C11D 3/48, 3/20, 3/12, 3/14 :510/131, 199, 382, 383, 319, 508; 424/409, 421, 618, 617	
According	to international Patent Classification (IPC) or to both national classification	and IPC
	ZLDS SEARCHED  documentation searched (classification system followed by classification symbols)	
U.S. :	510/131, 199, 382, 383, 319, 508; 424/409, 421, 618, 617	bols)
	ation searched other than minimum documentation to the extent that such docum	
,	data base consulted during the international search (name of data base and, w AS Online terms: silver, Ag, AgCl, detergents	there practicable, search terms used)
C. DO	CUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevan	nt passages Relevant to claim No.
Y	US 5,413,788 A (EDWARDS et al.) 09 May 199 line 54, through col. 5, line 20.	
Y	US 4,906,466 A (EDWARDS et al.) 06 March 199 line 6, through col. 4, line 56.	10, col. 3, 1-3
١.	US 5,334,588 A (FOX et al.) 02 August 1994.	
	US 5,180,585 A (JACOBSON et al.) 19 January 1	1993.
	US 4,952,411 A (FOX et al.) 28 August 1990.	
Furthe	r documents are listed in the continuation of Box C. See patent far	
Spec	al categories of cited documents	·
dacu to be	ment defining the general state of the est which is not set as a date and not in confi	whed after the interactional filing date or priority ict with the application but cited to tenderstand the meterlying the invention
doom	or document published on or after the international filing date. "X" document of particular terms which many them. A state of particular terms and the contract	the relevance; the claimed invention cannot be
4Pecis	I remon (as specified)  act referring to an oral disclosure, use, exhibition or other  considered to involve or other	her relevance; the claimed invention cannot be to an inventive step when the document is
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ashington, D simile No.	(703) 305-3230	1
PCT/ISA	7210 (second sheet)(July 1992)*	08-3805

#### INTERNATIONAL SEARCH REPORT

International application No. PCT/US96/20067

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)	_
This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:	
1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:	
Claims Nos.:     because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:	
Claims Nos.: 4-18     because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(s).	
Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)	
This International Searching Authority found multiple inventions in this international application, as follows:	
1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.	
<ol> <li>As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.</li> </ol>	
As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:	
No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:	
Remark on Protest  The additional search fees were accompanied by the applicant's protest.  No protest accompanied the payment of additional search fees.	